

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
**07.02.2001 Bulletin 2001/06**

(51) Int Cl.7: **C01B 3/50, F25J 3/00**

(21) Application number: **00306579.4**

(22) Date of filing: **02.08.2000**

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU**  
**MC NL PT SE**  
 Designated Extension States:  
**AL LT LV MK RO SI**

(72) Inventor: **McNeil, Brian Alfred**  
**Chessington, Surrey KT9 1PW (GB)**

(74) Representative: **Burford, Anthony Frederick**  
**W.H. Beck, Greener & Co.**  
**7 Stone Buildings**  
**Lincoln's Inn**  
**London WC2A 3SZ (GB)**

(30) Priority: **04.08.1999 GB 9918420**

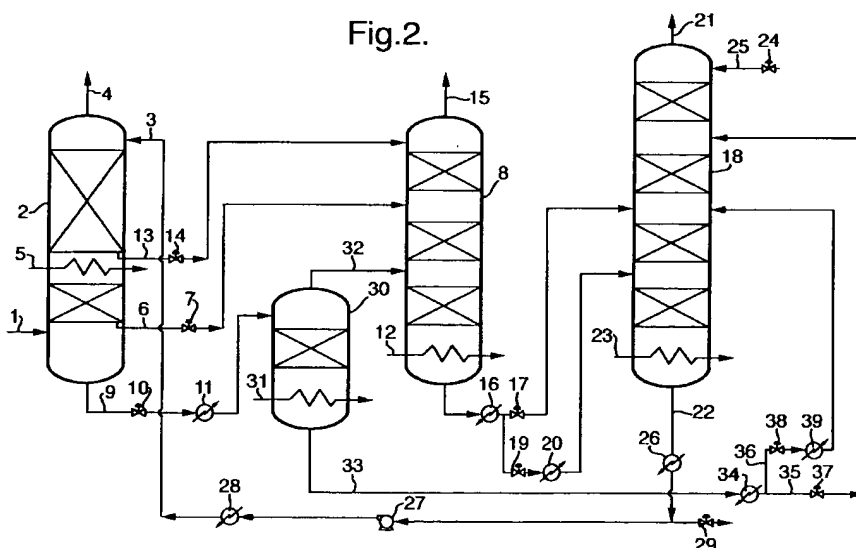
(71) Applicant: **AIR PRODUCTS AND CHEMICALS,**  
**INC.**  
**Allentown, PA 18195-1501 (US)**

(54) **Process and apparatus for separating mixtures of hydrogen and carbon monoxide**

(57) Hydrogen and carbon monoxide are separated from a condensate-containing gaseous mixture thereof by using (a) a ("first") stripping column (8) to remove the hydrogen content of the CO-loaded methane stream (6) obtained by washing CO from the gaseous mixture, or the vapour portion from a phase separation thereof, ascending a methane wash column (2) and (b) a ("second") stripping column or a flash separator (30) to remove the hydrogen content of the feed gas condensate (9) obtained from the methane wash column (2), or the phase separation. The vapour stream (32) from the sec-

ond stripping column or flash separator (30) is fed to the first stripping column (8). The liquid stream from the first stripping column and the liquid stream (33) from the second stripping column or flash separator (30) are fed (16, 17, 19 & 20; 34 to 39) to different locations of a separation column (18) providing a gaseous carbon monoxide product stream (21) and a liquid methane wash recycle stream (3). The process improves the efficiency of the separation by avoiding dilution of the CO concentration of the feed gas condensate (9) with the CO-loaded methane stream (6) which occurs in prior art CO/hydrogen separations using a methane wash.

**Fig.2.**



## Description

[0001] This invention relates to a process and apparatus for separation of hydrogen and carbon monoxide from gaseous mixtures thereof. It has particular, but not exclusive, application to the recovery of hydrogen and carbon monoxide from synthesis gas.

[0002] Carbon monoxide is usually obtained by separation from synthesis gas produced by catalytic conversion or partial oxidation of natural gas, oils or other hydrocarbon feedstock. Synthesis gas consists primarily of hydrogen and carbon monoxide and, depending on the level of purity, typically also contains small amounts of *inter alia* methane and nitrogen. It is well known to separate carbon monoxide from synthesis gas by a cryogenic separation process in which carbon monoxide is removed by a low temperature scrubbing step using liquid methane in a wash column to provide a CO-loaded methane liquid containing some, typically 2 to 4%, hydrogen. Residual hydrogen is removed from the CO-loaded methane liquid in, for example, a stripping column or flash separator to meet the required carbon monoxide product specification and the resultant hydrogen-stripped CO-loaded methane liquid is separated into a gaseous carbon monoxide product and liquid methane in a separation column. The bulk of the liquid methane is recycled to provide the methane wash liquid and a portion of the carbon monoxide product can be recycled to provide a heat pump stream.

[0003] The CO-loaded methane liquid can be withdrawn entirely from the sump of the methane wash column, in which case it is admixed with condensate from the feed gas. However, the condensate usually has a much higher CO concentration (typically 60 to 70% CO) than the CO-loaded methane (typically 20 to 30% CO), which higher concentration is diluted by admixture with the CO-loaded methane thereby decreasing the efficiency of the subsequent separation of CO from methane. In order to mitigate this reduction in potential efficiency, the CO-loaded methane can be separately withdrawn from a location above the synthesis gas feed and fed to a stripping column at a higher location than the feed gas condensate.

[0004] EP-A-0895961 discloses the separation of synthesis gas, or other gaseous mixtures of hydrogen and carbon monoxide, by a process in which the CO-loaded methane and feed gas condensate are separately fed from the methane wash column to vertically spaced locations of a stripping column. The stripping column is refluxed with a methane-rich scrubbing liquid withdrawn from an intermediate location of the methane wash column. Preferably, the hydrogen-stripped CO-loaded methane liquid is split into two substreams. One substream is subcooled and the subcooled liquid introduced into the separation column. The other substream is at least partially vaporised and introduced into the separation column at a location below that of the subcooled substream.

[0005] US-A-5133793 discloses the separation of synthesis gas, or other gaseous mixtures of hydrogen and carbon monoxide, by a process in which feed gas condensate is separated from the feed prior to the methane wash column. Only the vapour portion from that separation is fed to the wash column. The condensate is vaporised and fed to the stripping column at a location below that of the sump liquid from the wash column. The hydrogen-stripped CO-loaded methane liquid is subcooled and split into three substreams. One substream is introduced, at about its bulb temperature, at upper location of the separation column. Another substream is vaporised and introduced, at about its dew point, at a lower location of the separation column. The third substream is vaporised and introduced, at a temperature intermediate that of the other two substreams, at an intermediate location of the separation column.

[0006] Although the feeding of feed gas condensate to a stripping column separately from the CO-loaded methane does increase the efficiency with which hydrogen is removed in that column, it does not obviate the loss in potential efficiency in reduction of the CO concentration of the condensate on admixture with the CO-loaded methane. However, the necessity of this loss has been accepted in the art.

[0007] It is an object of the present invention to improve the efficiency of separation of carbon monoxide from a mixture with hydrogen. This is achieved by reducing the extent to which the CO concentration in the feed gas condensate is diluted prior to the separation of CO and methane.

[0008] Accordingly, in a first aspect of the invention, there is provided a process for separating hydrogen and carbon monoxide from a condensate-containing gaseous mixture thereof, said process comprising:

(a) scrubbing the gaseous mixture, or a vapour portion from phase separation thereof, with a liquid methane wash stream in a methane wash column to provide a gaseous hydrogen product stream and a liquid CO-loaded methane stream;

(b) separating said CO-loaded methane stream into a gaseous hydrogen-rich stream and a ("first") liquid CO/methane stream in a ("first") stripping column; and

(c) separating said first CO/methane stream into a gaseous carbon monoxide stream and a liquid methane stream in a separation column,

characterised in that feed gas condensate from the methane wash column, or from the phase separation, is separated into another ("second") gaseous hydrogen-enriched stream and another ("second") liquid CO/methane stream in another ("second") stripping column or a flash separator; the second gaseous hydrogen-enriched stream is fed to the

first stripping column; and the second liquid CO/methane stream is fed to the separation column.

[0009] In a second aspect of the invention there is provided an apparatus for separating hydrogen and carbon monoxide from a condensate-containing gaseous mixture thereof by a process of the first aspect, said apparatus comprising:

- (a) a methane wash column;
- (b) means for feeding the gaseous mixture to the methane wash column and optionally including phase separation means for removing a feed gas condensate from the gaseous mixture;
- (c) a ("first") stripping column;
- (d) a carbon monoxide/methane separation column;
- (e) means for feeding CO-loaded methane from the methane wash column to the first stripping column;
- (f) means for feeding liquid CO/methane from the first stripping column to the separation column; and
- (g) means for recycling liquid methane from the separation column to the methane wash column,

characterised in that the apparatus further comprises

- another ("second") stripping column or a flash separator;
- means for feeding feed gas condensate from the methane wash column, or from the phase separation means, to the second stripping column or flash separator;
- means for feeding a ("second") gaseous hydrogen-enriched stream from the second stripping column or flash separator to the first stripping column; and
- means for feeding a "second" liquid CO/methane stream from the second stripping column or flash separator to the separation column.

[0010] The invention has particular application to the separation of carbon monoxide from synthesis gas produced by catalytic conversion or partial oxidation of natural gas, oils or other hydrocarbon feedstock. However, it is of general application to the cryogenic separation of other gaseous mixtures containing hydrogen and carbon monoxide, especially those consisting primarily of hydrogen and carbon monoxide.

[0011] In a presently preferred embodiment, the condensate-containing gaseous mixture is fed to the methane wash column and the CO-loaded methane and feed gas condensate are separately removed from vertically spaced locations of said column. According to the alternative embodiment, the condensate-containing gaseous mixture is phase separated to provide the feed gas condensate; the uncondensed (vapour) portion is fed to the methane wash column; and the condensate is fed to the second stripping column or flash separator.

[0012] It is preferred that the feed gas condensate is partially vaporised before being fed to the second stripping column or flash separator.

[0013] The second liquid CO/methane stream can be split into at least two substreams; one substream being subcooled and the subcooled liquid introduced into the separation column and another substream being at least partially vaporised and introduced into the separation column at a location below that of the subcooled substream.

[0014] The first liquid CO/methane stream also can be split into at least two substreams; one substream being subcooled and the subcooled liquid introduced into the separation column and another substream being at least partially vaporised and introduced into the separation column at a location below that of said subcooled substream.

[0015] The first stripping column can be refluxed with a methane-rich liquid stream withdrawn from an intermediate location of the methane wash column above the level of removal of the CO-loaded methane therefrom as taught in EP-A-0895961 (the entirety of the disclosure of which is incorporated by this reference).

[0016] The present invention will now be described by way of example only with reference to the accompanying drawings in which:

Figure 1 is a schematic representation of a process and apparatus in accordance with the teaching of EP-A-0895961;

Figure 2 is a schematic representation of a preferred embodiment of the process and apparatus of the present invention; and

Figure 3 is a schematic representation of another embodiment of the process and apparatus of the invention.

[0017] The same reference numerals are used to identify the same or equivalent items in all three drawings.

[0018] Referring first to Figure 1, partially condensed crude synthesis gas is fed via conduit 1 to the bottom of methane wash column 2. The vapour rising up through the wash column trays or packing is scrubbed with liquid methane intro-

duced at the top of the column via conduit 3. This dissolves carbon monoxide into the liquid methane and produces an overhead hydrogen product in conduit 4. The heat of solution of carbon monoxide in the wash methane is typically removed by indirect heat exchange with at least part of a liquid carbon monoxide heat pump stream in heat exchanger (s) 5. This can typically be accomplished by at least one contactor heat exchanger as described in US-A-3,813,889 and is shown only schematically here. The number of contactor heat exchangers, their position and configuration within the methane wash column stages, is such as to most economically provide near isothermal operation of the column.

[0019] The CO-loaded methane from the bottom stage of the methane wash column, (which typically contains 2% to 4% H<sub>2</sub>), is removed via conduit 6, reduced in pressure by control valve 7, and introduced into stripping column 8, containing trays or packing, where hydrogen is stripped from the liquid in order to achieve the required carbon monoxide product purity specification. Condensate in the crude synthesis gas feed is removed from the sump of the methane wash column via conduit 9, reduced in pressure by control valve 10, and partly vaporised in heat exchanger 11, preferably by indirect heat exchange with at least part of the crude synthesis gas upstream of conduit 1. Alternatively other heat exchange means could be provided. The partly vaporised liquid is then fed to stripping column 8 several stages below the introduction of the liquid in conduit 6 to provide part of the stripping vapour for hydrogen removal from the latter stream. A reboiler 12 in the bottom of the stripping column 8 provides stripping vapour for the liquid in both feed streams. The liquid introduced via conduit 6 also serves to scrub some of the carbon monoxide from the vapour passing through the hydrogen stripping column. A methane rich scrubbing liquid is withdrawn from an appropriate stage of the methane wash column via conduit 13, reduced in pressure by control valve 14, and used to provide wash liquid to the top of the stripping column 8 to further reduce carbon monoxide losses in the reject hydrogen stream from conduit 15.

[0020] Liquid from the bottom of the stripping column 8 is subcooled in heat exchanger 16 and then divided into two substreams. The first substream is reduced in pressure by control valve 17, and introduced to carbon monoxide/methane separation column 18. The second substream is reduced in pressure by control valve 19, partially vaporised in heat exchanger 20, and introduced to separation column 18 several stages below the subcooled liquid from control valve 17. The two feeds are separated in separation column 18 into carbon monoxide and methane streams in conduits 21 and 22 respectively. The column 18 is reboiled by reboiler 23, and reflux is provided by direct introduction of liquid carbon monoxide via control valve 24 and conduit 25. Heat transfer in heat exchangers 16 and 20 is accomplished by indirect heat exchange with other process streams and is not detailed here.

[0021] Purified methane liquid in conduit 22 is subcooled in subcooler 26 by indirect heat exchange with other process streams, not detailed here, and then divided. The major part of stream 22 is pumped by pump 27 to methane wash column pressure, further subcooled in heat exchanger 28, and introduced to the top of the methane wash column 2 via conduit 3. The minor portion of stream 22 is removed from the distillation system via control valve 29.

[0022] Table 1 summarises a mass balance for a typical application of the process of Figure 1.

TABLE 1

Stream		1	3	4	6	9	13	15	21	22	25
Pressure	bar(a)	21.7	22.6	21.4	21.6	21.6	21.5	5.5	2.8	3.0	2.8
Temperature	deg C	-180	-181	-181	-173	-180	-178	-166	-182	-146	-182
Flowrate	kgm/h	100.0	39.0	69.4	49.0	17.5	3.0	2.8	31.7	42.9	7.9
Hydrogen	mol %	70.3		98.7	2.2	3.6	1.8	62.5			0
Nitrogen	mol %	1.4		0.2	1.4	3.1	2.2	4.2	5.0		5 0
Carbon monoxide	mol %	23.2			23.0	66.8	7.1	21.4	95.0		95.0
Methane	mol %	5.0	100	1.1	73.3	26.4	89.0	11.9		100.0	0
Vapour fraction		0.8232	0	1	0	0	0	1	1	0	0.0462

[0023] Referring now to Figure 2, the illustrated preferred embodiment of the invention differs from the process and apparatus of Figure 1 in that the partially vaporised condensate from heat exchanger 11 is fed to the top of second stripping column 30. This column 30 contains trays or packing and reboiler 31 in the bottom of the column provides stripping vapour to strip hydrogen from the liquid in order to achieve the required CO product purity specification. Vapour from second stripping column 30 is fed via conduit 32 to stripping column 8 several stages below the introduction of the CO-loaded methane from conduit 6 to provide part of the stripping vapour for hydrogen removal from the CO-loaded methane.

[0024] Liquid in conduit 33 from the bottom of the second stripping column 30 is subcooled in heat exchanger 34 and divided into two substreams 35 and 36. Substream 35 is reduced in pressure by control valve 37, and introduced to column 18 several stages above the subcooled liquid from control valve 17. Substream 36 is reduced in pressure by control valve 38, partially vaporised in heat exchanger 39, and introduced to column 18 at about the same location as the subcooled liquid from control valve 17. The four feeds are separated in column 18 into the purified CO and methane streams in conduits 21 and 22 respectively. Heat transfer in heat exchangers 34 and 39 is accomplished by indirect heat exchange with other process streams and is not detailed here.

[0025] Table 2 summarises a mass balance for a typical application of the process of Figure 2.

TABLE 2

Stream		1	3	4	6	9	32	13	15	21	22	25
Pressure	bar (a)	21.7	22.6	21.4	21.6	21.6	5.6	21.5	5.5	2.8	3.0	2.8
Temperature	deg C	-180	-181	-181	-173	-180	-168	-178	-167	-182	-146	-182
Flowrate	kgm/h	100.0	39.1	69.4	48.2	17.5	7.4	3.9	2.8	30.3	43.0	6.5
Hydrogen	mol %	70.3		98.7	2.2	3.6	8.6	1.8	62.4			
Nitrogen	mol %	1.4		0.1	1.4	3.1	4.6	2.1	4.7	5.0		5.0
Carbon monoxide	mol %	23.2			23.3	66.8	80.8	7.2	21.3	95.0		95.0
Methane	mol %	5.0	100.0	1.1	73.0	26.4	6.0	88.9	11.5		100.0	
Vapour fraction		0.8232	0	1	0	0	1	0	1	1	0	0.0462

[0026] Referring now to Figure 3, another embodiment of the present invention differs from that of Figure 2 in that condensate is separated from the feed 1 by a phase separator 40 and only the vapour portion fed to the wash column 2 via conduit 41. The CO-loaded methane and any condensate from the vapour portion feed is withdrawn from the sump of the column 2 and fed, via conduit 6 and control valve 7, to stripping column 8. The condensate separated in phase separator 40 is fed, via conduit 9, control valve 10 and heat exchanger 11, to the second stripping column 30.

[0027] Table 3 summarises a mass balance for a typical application of the process of Figure 3.

10

15

20

25

30

35

40

45

50

55



TABLE 3

Stream		1	3	4	6	9	32	13	15	21	22	25
Pressure	bar (a)	21.7	22.6	21.4	21.6	21.6	5.6	21.5	5.5	2.8	3.0	2.8
Temperature	deg C	-180	-181	-181	-173	-180	-168	-178	-167	-182	-146	-182
Flowrate	kgm/h	100.0	39.1	69.4	48.2	17.5	7.4	3.9	2.8	30.3	43.0	6.5
Hydrogen	mol %	70.3		98.7	2.2	3.6	8.6	1.8	62.4			
Nitrogen	mol %	1.4		0.1	1.4	3.1	4.6	2.1	4.7	5.0		5.0
Carbon monoxide	mol %	23.2			23.3	66.8	80.8	7.2	21.3	95.0		95.0
Methane	mol %	5.0	100.0	1.1	73.0	26.4	6.0	88.9	11.5		100.0	
Vapour fraction		0.8232	0	1	0	0	1	0	1	1	0	0.0462

[0028] It will be appreciated that the invention is not restricted to the specific details described above with reference to Figures 2 and 3 but that numerous modifications can be made without departing from the invention as defined in the following claims. For example, one or more of the following modifications can be made to the process and apparatus of either Figure 2 or Figure 3:

the second stripper 30 could be replaced by a flash separator;  
 the methane wash could be omitted from the stripping column 8;  
 the CO-loaded methane in conduit 6 could be preheated by indirect heat exchange after pressure reduction via valve 7;  
 one or more of heat exchangers 11, 16, 20, 34, and 39 could be omitted;  
 one of heat exchangers 26 and 28 could be omitted; and  
 heat of solution could be removed by indirect heat exchange with at least part of a heat pump stream in a contactor heat exchanger located at the top of the stripping column 8 to achieve higher CO recovery or reduce the quantity of methane rich liquid used for washing.

[0029] It will be appreciated from the preceding description of the present invention that it differs from the prior art by utilising a second stripper column or a flash separator to reject hydrogen, thus keeping the CO-richer condensed feed liquid separate from the CO-leaner methane wash column liquid. The invention therefore benefits by reducing the energy required for CO/methane separation. Consequently the recycle heat pump flowrate that is required for the regeneration column separation is reduced, resulting in a compressor power reduction of about 3% to 5%.

### Claims

1. A process for separating hydrogen and carbon monoxide from a condensate-containing gaseous mixture thereof, said process comprising:

- (a) scrubbing the gaseous mixture, or a vapour portion from phase separation thereof, with a liquid methane wash stream in a methane wash column to provide a gaseous hydrogen product stream and a liquid CO-loaded methane stream;
- (b) separating said CO-loaded methane stream into a gaseous hydrogen-rich stream and a ("first") liquid CO/methane stream in a ("first") stripping column; and
- (c) separating said first CO/methane stream into a gaseous carbon monoxide stream and a liquid methane stream in a separation column,

characterised in that

feed gas condensate from the methane wash column or the phase separation is separated into another ("second") gaseous hydrogen-enriched stream and another ("second") liquid CO/methane stream in another ("second") stripping column or a flash separator;  
 the second gaseous hydrogen-enriched stream is fed to the first stripping column; and  
 the second liquid CO/methane stream is fed to the separation column.

- 2. A process as claimed in Claim 1, wherein said gaseous mixture consists primarily of hydrogen and carbon monoxide.
- 3. A process as claimed in Claim 2, wherein said gaseous mixture is synthesis gas produced by catalytic conversion or partial oxidation of natural gas, oils or other hydrocarbon feedstock.
- 4. A process as claimed in any one of the preceding claims, wherein the condensate-containing gas mixture is fed to the methane wash column and the CO-loaded methane and feed gas condensate are separately removed from vertically spaced locations of said column.
- 5. A process as claimed in any one of Claims 1 to 3, wherein the condensate-containing gas mixture is phase separated to provide said feed gas condensate; the uncondensed (vapour) portion is fed to the methane wash column; and the condensate is fed to the second stripping column or flash separator.
- 6. A process as claimed in any one of the preceding claims, wherein the condensate is partially vaporised before

being fed to the second stripping column or flash separator.

7. A process as claimed in any one of the preceding claims, wherein the second liquid CO/methane stream is split into at least two substreams; one substream is subcooled and the subcooled liquid introduced into the separation column and another substream is at least partially vaporised and introduced into the separation column at a location below that of the subcooled substream.

8. A process as claimed in any one of the preceding claims, wherein the first liquid CO/methane stream is split into at least two substreams; one substream is subcooled and the subcooled liquid introduced into the separation column and another substream is at least partially vaporised and introduced into the separation column at a location below that of said subcooled substream.

9. A process as claimed in any one of the preceding claims, wherein the first stripping column is refluxed with a methane-rich liquid stream withdrawn from an intermediate location of the methane wash column above the level of removal of the CO-loaded methane therefrom.

10. An apparatus for separating hydrogen and carbon monoxide from a condensate-containing gaseous mixture thereof by a process of the first aspect, said apparatus comprising:

- (a) a methane wash column (2);
- (b) means (1) for feeding the gas mixture to the methane wash column and optionally including phase separation means (40) for removing feed gas condensate from the gaseous mixture;
- (c) a ("first") stripping column (8);
- (d) a carbon monoxide/methane separation column (18);
- (e) means (6 & 7) for feeding CO-loaded methane from the methane wash column (2) to the first stripping column (8);
- (f) means (16, 17, 19 & 20) for feeding liquid CO/methane from the first stripping column (8) to the separation column (18); and
- (g) means (22, 26, 27, 28 & 3) for recycling liquid methane from the separation column (18) to the methane wash column (2),

characterised in that the apparatus further comprises

- another ("second") stripping column or a flash separator (30);
- means (9 & 11) for feeding feed gas condensate from the methane wash column (2) or the phase separation means (40) to the second stripping column or flash separator (30);
- means (9 & 11) for feeding a ("second") second gaseous hydrogen-enriched stream from the second stripping column or flash separator (30) to the first stripping column (8); and
- means (33 to 39) for feeding a "second" liquid CO/methane stream to the separation column (18).

11. An apparatus as claimed in Claim 10, wherein the means (1) for feeding the gas mixture to the methane wash column (2) does not include the optional phase separation means (40); the means (9 & 11) for feeding feed gas condensate to the second stripping column or flash separator (30) extends from the sump of the wash column (2); and the means (6 & 7) for feeding CO-loaded methane to the first stripping column (8) extends from a location of the wash column (2) above the feed thereto.

12. An apparatus as claimed in Claim 10, wherein the means (1) for feeding the gas mixture to the methane wash column includes the optional phase separation means (40); the means (9 & 11) for feeding feed gas condensate to the second stripping column or flash separator (30) extends from the phase separation means; and the means (6 & 7) for feeding CO-loaded methane to the first stripping column (8) extends from the sump of the wash column (2).

13. An apparatus as claimed in any one of Claims 10 to 12, wherein there is further provided heat exchange means (11) for partially vaporising the condensate before being fed to the second stripping column or flash separator (30).

14. An apparatus as claimed in any one of Claims 10 to 13, wherein there is further provided means (34 & 37) for subcooling a substream (35) of the second liquid CO/methane stream (33) and feeding the subcooled liquid to the separation column (18) and means (38 & 39) for at least partially vaporising a second substream (36) of the second

liquid CO/methane stream (33) and feeding the at least partially vaporised substream to the separation column (18) at a location below that of the subcooled substream (35).

15. An apparatus as claimed in any one of Claims 10 to 14, wherein there is further provided means (16 & 17) for subcooling a substream of the first liquid CO/methane stream and feeding the subcooled liquid to the separation column (18) and means (19 & 20) for at least partially vaporising a second substream of the first liquid CO/methane stream and feeding the at least partially vaporised substream to the separation column (18) at a location below that of said subcooled substream.

Fig.1.

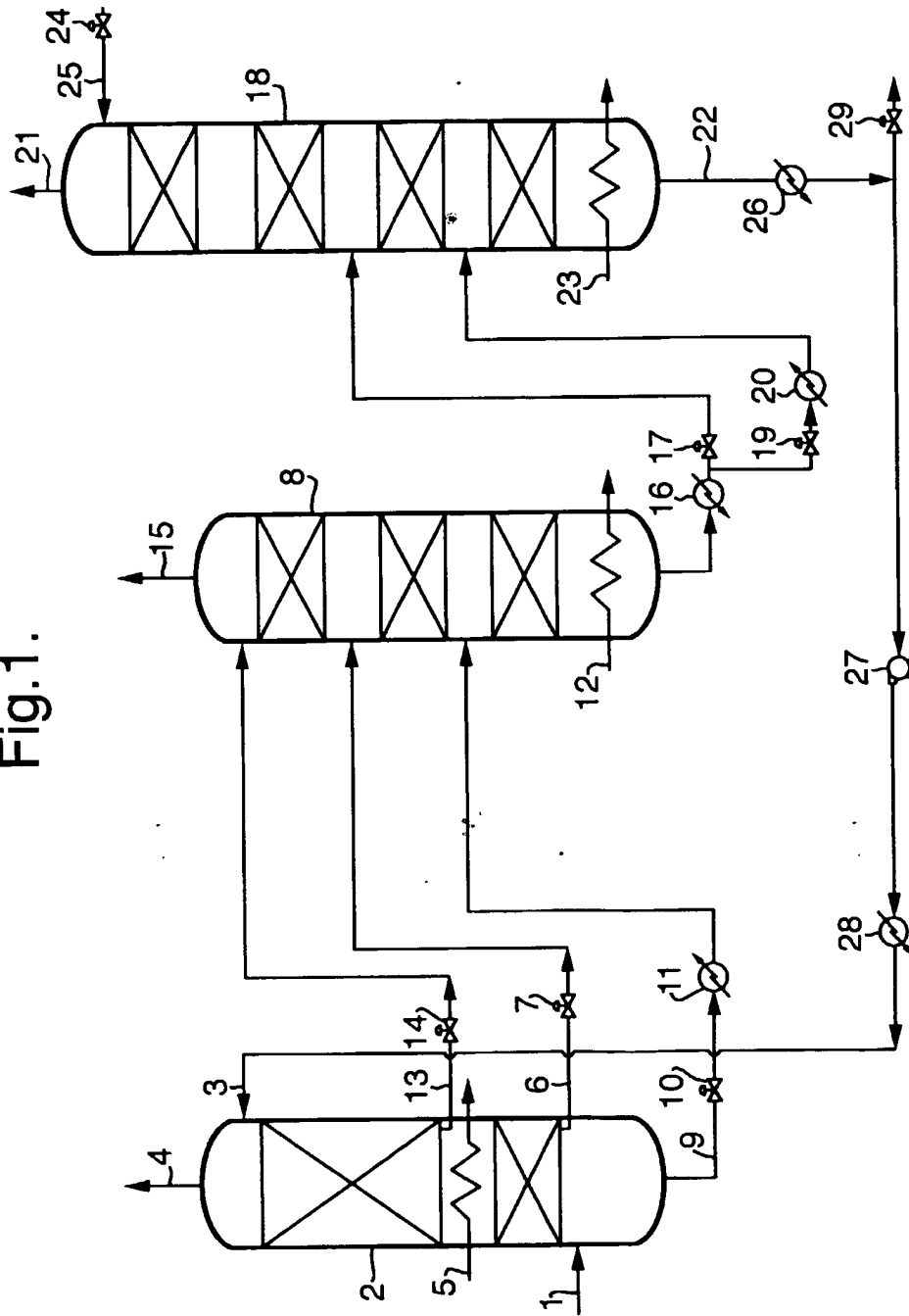


Fig.2.

